SPECIFICATION

Docket No. TA-00496

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN that I, Slade H. Gardner, have invented new and useful improvements in a

Method of Forming Ecoceramic-Based Silicon-Carbide Tooling for Composites and Method for Forming Composites Using Same

of which the following is a specification:

"EXPRESS MAIL" NO. ***EL 871043624 US***

I hereby certify that this paper or fee is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10 on the date indicated below and is addressed to the Hon. Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Date of Deposit: Jan. 11, 2002 By: Sarah Garner

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates generally to forming silicon-carbide tooling and relates specifically to forming tooling used for layup and curing of composite structures.

2. Description of the Prior Art

[0002] Tooling for production of composite aircraft parts have close tolerances for dimensional control and are typically made from invar alloy. Invar can be characterized as an expensive material which is difficult to machine. However, an attractive feature of invar is a very low coefficient of thermal expansion (CTE) of approximately 1.5 μin./in./°F at temperatures up to 400°F. For applications such as making flat laminates, other tooling materials are sometimes used, including aluminum and steel, and have CTE values of approximately 14 μin./in./°F and 7 μin./in./°F, respectively.

[0003] A low CTE is necessary for producing high-temperature-cure polymer-matrix/carbon-fiber composites with precise dimensional accuracy. A mismatch in the CTE of the composite material and the tooling material will cause complications for maintaining dimensional accuracy. The CTE of a typical polymer-matrix/carbon-fiber composite is difficult to characterize precisely because it is a multi-component system. Carbon fiber has a small, negative CTE and a typical polymer matrix systems for structural aircraft composite components have a CTE in the range of 15-50 μin./in./°F. The CTE of a specific composite system will be dependent upon the lay-up construction and the composition.

[0004] Recently, technology has been developed at NASA Glenn Research Center to produce very economical, complex-shaped, silicon carbide (SiC) ceramic structures from wood precursors, called "ecoceramics." To produce the ceramics, a wood preform is pyrolyzed in an inert atmosphere to convert the organic material into a carbonaceous form. The preform is infused with liquid silicon

or silicon alloy, and the infiltrated preform is converted to a SiC in a high temperatures furnace. These materials have tailorable microstructures, low manufacturing costs, and can be easily machined in precursor stage before forming near-net shape ceramic structures. The targeted applications for this material have been seals, rings and filters for automotive applications; and armor, bricks, foundry crucibles and furnace components. These applications make use of the high service temperature of SiC (1350°C).

[0005] One limitation of the NASA process, however, is that it is limited to small pieces of wood, especially those having a thickness of less than 1 in. With larger pieces of wood, cracking and warping are caused as the wood is dried and pyrolyzed, causing loss of tolerance and defects in the structure.

[0006] It is generally accepted that a material having a low CTE is desirable for use as composite tooling, and the CTE of SiC is approximately 2.5 μin./in./°F in the temperature range of 70-2282°F. There exists a need for low-cost, easily-manufactured, SiC tooling for use in forming composite components of many sizes and thicknesses.

SUMMARY OF THE INVENTION

[0007] A method is provided for forming items from ecoceramic-based silicon-carbide. A wood preform is machined to a general shape having over- or undersized dimensions. The preform is pyrolyzed to transform the wood of the preform to a porous, carbonaceous material that retains the general shape of the preform. The preform is then machined to final, net-shape dimensions and immersed in liquid silicon or silicon alloy that penetrates and infuses the preform. The infused preform is held at a temperature sufficient to cause the transformation of the material in the preform to silicon carbide, completing formation of the item. Also provided is a method of forming ecoceramic-based tooling and composite components using the tooling.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The novel features believed to be characteristic of the invention are set forth in the appended claims. The invention itself however, as well as a preferred mode of use, further objects and advantages thereof, will best be understood by reference to the following detailed description of an illustrative embodiment when read in conjunction with the accompanying drawings.

[0009] **Figure 1** is a perspective view of a wooden preform for use in producing a tool in accordance with the present invention.

[0010] **Figure 2** is a perspective view of the wooden preform of FIG. 1 after the first machining step of the method of the present invention.

[0011] **Figure 3** is a perspective view of the preform of FIG. 1 after the pyrolyzing step of the method of the present invention.

[0012] **Figure 4** is a perspective view of the preform of FIG. 1 after the additional machining step of the method of the present invention.

[0013] **Figure 5** is a schematic end view of the preform of FIG. 1 immersed in liquid silicon according to the method of the present invention.

[0014] **Figure 6** is a perspective view of an ecoceramic tool formed from the preform of FIG. 1 and in accordance with the present invention.

[0015] **Figure 7** is a flowchart depicting the steps of a method of the present invention.

[0016] **Figure 8** is a perspective view of the tool of FIG. 6 after application of a mold release.

[0017] **Figure 9** is a perspective view of the tool of FIG. 6 with a composite component being formed on the tool.

DETAILED DESCRIPTION OF THE INVENTION

[0018] FIG. 1 shows a wood preform 11, which may be formed from one of several varieties of trees, e.g., black walnut or maple. As shown in the figures, preform 11 is a rectangular solid, though preform 11 may be of any shape capable of withstanding the process described below. Preform 11 has an upper surface 13 into which a recess 15 is machined, recess 15 having a rough, general shape of the desired negative mold, as shown in FIG. 2. The negative mold is machined to have undersized dimensions, allowing for machining to the desired dimensions of the finished mold after subsequent steps. As illustrated in FIG. 2, the rough shape of recess 15 lacks the smooth contours of the desired shape (shown in FIGS. 4 and 6). Because wood is relatively soft when compared to normal tooling materials, such as invar alloy, machining preform 11 is quick and causes little wear on the tools used in the machining process. Though not shown, a positive mold would require an oversized rough shape to provide for additional material to be machined in later steps.

[0019] Once recess 15 is cut into preform 11, preform 11 is pyrolyzed in an inert atmosphere. To prevent combustion of preform 11, an inert gas, preferably argon, is used within the furnace, the argon displacing oxygen-rich air. Because preform 11 has moisture within it, preform 11 is first slowly dried to prevent cracking of preform 11 that could occur during pyrolyzation.

[0020] The preferred method of drying preform 11 involves covering preform 11 with a vacuum bag, applying vacuum to the bag, then placing the bagged preform11 in a pressurized autoclave and increasing the temperature within the autoclave. For example, the temperature in the autoclave is raised at up to 10°C per minute to a temperature of 90°C to 120°C, where it is held for several hours, allowing for moisture to be removed without damage to preform 11. The pressurized atmosphere minimizes the temperature gradients in the autoclave and in preform 11, which reduces the chance of preform 11 warping during drying. Also, the pressurized atmosphere within the autoclave, which may be up to 90psi of nitrogen, applies pressure to the outer surfaces of preform 11, reducing the amount of cracking occurring in larger preforms 11. The vacuum bag allows for negative pressure to be applied to preform 11, enhancing the process of moisture removal prior to the water turning to steam, which may cause cracking of preform 11.

[0021] The drying step may also be divided into two steps to avoid cracking in thick preforms 11. For example, the autoclave may be raised to approximately 90°C and held for 2 hours to 24 hours for an initial drying. For best results, vacuum should be applied to the bag at the beginning of the cycle. Then the temperature can be raised at up to 1°C per minute to between 100°C and 120°C and held for an additional 2 hours to 24 hours, ensuring a complete drying of preform 11.

[0022] The next step is to remove preform 11 from the autoclave, remove the vacuum bag, then replace preform 11 in the autoclave with a pressurized nitrogen atmosphere, preferably 15psi to 90psi. The pressure in the autoclave minimizes thermal gradients in the autoclave and provides increased hydrodynamic pressure to maintain the dimensional stability of preform 11. The temperature within the autoclave is slowly increased again at up to 5°C per minute to preferably between 100°C and 120°C and is held for 1 hour to 10 hours, then is preferably ramped upward to 220°C at the rate of approximately 0.28°C per minute.

[0023] When preform 11 approaches 220°C, an oily residue, referred to as bio-oil, and vapors begin to emerge from preform 11. Bio-oils are a mixture of chemicals resulting from the decomposition of organic matter within the wood of preform 11. The vacuum bag is removed before this step to prevent bio-oil and vapors from entering vacuum lines and to obviate the need for providing bleed cloths within the bag to absorb the bio-oil as it is produced.

[0024] Once the temperature has reached 220°C, the rate of increase of the temperature is preferably reduced to approximately 0.17°C per minute until the temperature reaches between 375°C and 425°C, though the rate may be up to 1°C per minute. Preform 11 is preferably held at approximately 400°C for 1 hour to 10 hours, the ambient pressure assisting in extracting the bio-oil. Afterward, preform 11 is removed from the autoclave, cooled, then inserted into a furnace where preform 11 is heated to a higher temperature than in the autoclave.

[0025] The furnace preferably has a constantly-flowing argon or nitrogen atmosphere at 1psig to 10 psig. The temperature in the furnace is raised to approximately 400°C at 1°C to 5°C per minute, then held from 1 hour to 10 hours. The temperature is then raised to between 900°C and

1100°C at a rate of up to 1°C per minute, and preform 11 is held at that temperature for approximately 1 hour to 10 hours. Preform 11 is then cooled to room temperature at a rate of approximately 1°C to 5°C, preferably under constantly flowing nitrogen or argon.

[0026] At this point, all of the material within preform 11 is completely pyrolyzed. The entire pyrolyzation process may take approximately 90 hours, though the time may be longer or shorter for different woods, thicknesses, shapes, etc. A pyrolyzed preform 11 is shown in FIG. 3, a lower corner having been removed to reveal the carbonaceous, foam-like material remaining in preform 11.

[0027] After pyrolyzing preform 11, recess 15 in upper surface 13 is machined to net-shape dimensions. By machining again after the pyrolyzation, dimensional changes in recess 15 caused by the pyrolyzation can be accounted for while also removing the additional material in recess 15 due to the undersize dimensions. FIG. 4 shows recess 15 as having the desired smooth contours of the finished mold. The machining of the pyrolyzed preform 11 requires very little effort and causes little to no wear on machine tools.

[0028] To provide silicon and convert preform 11 into a SiC material, pyrolyzed preform11 is immersed in a tank 17 containing liquid silicon or silicon alloy 19, shown in FIG. 5. Preform 11 is held in tank 17 and at a temperature from approximately 900°C to 1450°C for 20 to 90 minutes. Liquid silicon 19 is drawn into preform 11 by capillary action, filling the micropores of preform 11. The infusion may also be assisted by vacuum. Liquid silicon 19 readily infiltrates the pores of preform 11, where the silicon reacts with the carbon of preform 11 to form SiC. If a silicon alloy, such as silicon-refractory metal alloys, is used, refractory disilicide is precipitated as the silicon reacts with the carbon. In either case, the final result is a dense matrix comprising silicon carbide and some free silicon or, in the case of alloy infiltration, some additional precipitated disilicide.

[0029] FIG. 6 shows the finished tool 21 formed from preform 11. A corner of tool 21 has been removed to illustrate the ceramic structure throughout tool 21. While it is desirable for recess 15 to have net-shape dimensions after the immersion and heating steps, some machining may be

required to dimension recess 15 to within desired tolerances. After typical tooling preparation, tool 21 may be used to form components from composite materials.

[0030] FIG. 7 shows a flowchart containing the steps for creating a composite layup tool using the method described above. In addition, the method includes layup of a composite component as an optional last step of the method. The step of block 23 is the rough shaping of the preform, which is then vacuum bagged and heated in an autoclave, as described in block 25. In the step of block 27, the bag is removed, and the preform is heated to a higher temperature, preform releasing vapors and bio-oil. The preform is completely pyrolyzed in the step of block 29, then preform is machined to net-shape dimensions in the step of block 31. The step of block 33 is the immersion of the preform in liquid silicon at approximately 900°C to 1450°C to cause the formation of SiC. These steps may be used to form any type of ecoceramic part, component, or tooling, and the step of block 35 provides for layup of composite parts on the tooling, as shown in FIGS. 7 and 8.

[0031] To prevent composite components formed on tool 21 from adhering to upper surface 13 and mold details such as recess 15, a mold release, or mold sealant, is applied to upper surface 13, as shown in FIG. 7. Mold release may be a wax or other form of release that coats surface 13 to limit the difficulty of removal of a composite component after the resin in the component is cured.

[0032] FIG. 8 shows a composite component 37 being formed on tool 21. Component 37 is formed from composite materials, typically multiple layers of woven fabric, though other types of fiber layers may be used, for example, fiber mats having short fibers in random orientations. The layers are preferably impregnated with an uncured resin prior to layup, but resin may be brushed on or otherwise applied to dry layers after each layer is placed on tool 21. Layers of component 37 are laid on surface 13, conforming to the contours of recess 15. A debulking process may be performed during layup to remove excess resin and to compact the layers. After the desired number of layers is applied, component 37 is cured while remaining on tool 21, curing typically occurring within an autoclave or other type of oven. Component 37 is then removed from tool 21.

[0033] The advantages of using the present invention to form large ecocermic components, such as large tooling structures, is that limitations to the size of wood preforms are determined only by the size of the furnaces used, not by the cracking or warping problems of prior methods. Furnaces exist which are large enough to accommodate any current composite tooling structure used in aerospace manufacturing. Also, techniques have been developed for joining multiple SiC components using the same heating process that converts the infused carbonaceous material to SiC. Therefore, very complex tooling structures can be formed from several pieces.

[0034] There are several advantages to using ecoceramics for composite tooling. Since all the machining is done in the wood or the carbonized state of the material, ecoceramics provide a faster and more economical alternative to machining tooling from metal, especially when considering the difficulty in machining invar alloy. Silicon and silicon alloys are inexpensive materials, and heating costs are relatively insignificant. The ecoceramic material has other advantages over the traditional tooling materials in that it is more dent resistant, can be repaired, and has a capability of withstanding higher temperatures.

[0035] While the invention has been shown in only one of its forms, it should be apparent to those skilled in the art that it is not so limited but is susceptible to various changes without departing from the scope of the invention. For example, wood particles, such as sawdust, can be mixed with binders and used to form the preform. The binders are carbonized along with the wood during the pyrolyzation step.